

# Configuration-averaged 4f orbitals in *ab initio* calculations of low-lying crystal field levels in lanthanide(III) complexes

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(Dated: 8 June 2016)

A successful and commonly used *ab initio* method for the calculation of crystal field levels and magnetic anisotropy of lanthanide complexes consists of spin-adapted state-averaged CASSCF calculations followed by state interaction with spin-orbit coupling (SI-SO). Based on two observations valid for Ln(III) complexes, namely: (i) CASSCF 4f orbitals are expected to change very little when optimized for different states belonging to the 4f electronic configuration, (ii) due to strong spin-orbit coupling the total spin is not a good quantum number, we show here via a straightforward analysis and direct calculation that the CASSCF/SI-SO method can be simplified to a single configuration-averaged HF calculation and one complete active space CI diagonalization, including spin-orbit coupling, on determinant basis. Besides its conceptual simplicity, this approach has the advantage that all spin states of the 4f<sup>n</sup> configuration are automatically included in the SO coupling, thereby overcoming one of the computational limitations of the existing CASSCF/SI-SO approach. As an example, we consider three isostructural complexes [Ln(acac)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>], Ln = Dy<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup>, and find that the proposed simplified method yields crystal field levels and magnetic g-tensors that are in very good agreement with those obtained with CASSCF/SI-SO.

## I. INTRODUCTION

The ability of single-molecule magnets (SMMs) to display long-lived spin-polarized states, which are of interest for the development of molecular magnetic memories, is fundamentally rooted in the details of the electronic structure of the ground state and the first few excited states of open-shell metal complexes.<sup>1</sup> In particular, complexes of trivalent lanthanide ions have recently proven to be promising to achieve SMM behavior at higher temperatures than their transition metal analogues.<sup>2–4</sup> One characteristic feature of the electronic structure of lanthanide complexes is that the lowest energy electronic states do not differ significantly from purely ionic states, leading to wave functions that are dominated by spin-orbit atomic *J*-multiplets weakly split by the crystal field potential of the surrounding ligands. This leads to unquenched 4f orbital angular momentum in the ground state, making the magnetism of the open shell 4f electrons particularly sensitive to the surrounding low-symmetry electrostatic environment via strong spin-orbit coupling, therefore often strongly anisotropic. The resulting magnetic anisotropy in turn can lead to a high spin-reorientation energy barrier in these complexes, which is at the origin of slow magnetic relaxation dynamics and SMM behavior.<sup>1</sup>

*Ab initio* calculations have proven very useful to help unravel the crucial magneto-structural correlations that characterize new or potential lanthanide SMMs.<sup>5–7</sup> The only *ab initio* method currently used for this purpose is a combination of the complete active space self consistent field method and the state interaction with spin-orbit coupling method,<sup>6</sup> which usually goes by the acronym

CASSCF/RASSI-SO in the literature, after its implementation in the MOLCAS software package.<sup>8,9</sup> We shall use the shorter name CASSCF/SI-SO in this paper.

One of the first successful applications of the CASSCF/SI-SO method to the magnetism of Ln(III) complexes was the explanation of a non-magnetic ground state Kramers doublet in a triangular Dy(III) cluster.<sup>10</sup> The calculations predicted that the local magnetic anisotropy of the Dy centers could be described by Ising-type spins whose local axes are tangential to the triangle, resulting in a net cancellation of the total magnetic moment. Subsequent studies used angle-dependent magnetic susceptibility measurements on single crystals to provide direct evidence that such calculations are indeed able to predict the direction of the magnetic easy axes and associated g-factors in a number of low-symmetry Ln(III) complexes.<sup>11–16</sup> Besides information on magnetic anisotropy, these *ab initio* calculations also provide crystal field energy levels which can be compared with experimental values, accessible through spectroscopic techniques.<sup>17,18</sup> CASSCF/SI-SO calculations have also been used to rationalize the direction and extent of the magnetic anisotropy in terms of ligand geometry and crystal field models based on electrostatic charge distributions,<sup>19–23</sup> to guide the design of new lanthanide-SMM candidates,<sup>24</sup> and to investigate spin and orbital magnetization densities in a series of lanthanide sandwich complexes.<sup>25</sup>

CASSCF/SI-SO is now widely used to compute spectroscopic and magnetic properties of Ln(III) complexes. Here we present a critical assessment of this approach and propose an alternative which is both a simplification and extension. Section II reviews how CASSCF/SI-SO is applied to Ln(III) complexes. A discussion of the characteristic electronic structure of 4f elements suggests that state-dependent orbital flexibility, provided by CASSCF, is of minor importance. This is corroborated

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by an analysis of the common practice of applying state-averaged CASSCF to these systems. Based on these findings we propose a simplified method based on one set of molecular orbitals, obtained from a configuration-averaged Hartree-Fock (CAHF) calculation. This approach allows a great simplification of the subsequent state-interaction problem, which can now be formulated as a simultaneous diagonalization of Coulomb repulsion and spin-orbit coupling in the basis of Slater determinants of the  $4f^n$  configuration (CASSCF-SO).

In order to test the CAHF/CASSCF-SO approach we apply it to three example complexes. Some technical details of the method are described in Section III. Section IV compares the results with those obtained with CASSCF/SO and it is shown that a very good agreement is found.

## II. CASSCF/SO TREATMENT OF THE ELECTRONIC STRUCTURE OF LN(III) COMPLEXES

We begin by reviewing the CASSCF/SO method as it is applied to mononuclear Ln(III) complexes in the molecular magnetism literature. (See, for example, Ref.<sup>6</sup> and references therein.)

The purpose of the CASSCF step is to obtain wave functions that can be thought of as corresponding to the atomic Russell-Saunders terms, whose degeneracies are weakly split by the presence of the ligand environment. For a Ln(III) complex whose formal configuration is  $4f^n$ , this is achieved by choosing the active space to consist of  $n$  electrons in the seven  $4f$ -like orbitals, giving rise to  $\binom{14}{n}$  Slater determinants. These are spin-adapted into configurational state functions (CSF) of definite spin quantum numbers  $S$ . For each spin manifold a number of CASSCF wave functions is then optimized. Spin-orbit coupling (SOC) is introduced in the second step (SO) by diagonalizing the SOC operator in the basis of the optimized CASSCF wave functions. The resulting eigenvectors are then used to calculate expectation values of relevant operators, in particular the magnetic moment.

Due to the importance of SOC in the rare-earth coupling scheme known from atomic theory, according to which the strengths of terms in the Hamiltonian are ordered as follows: interelectronic repulsion  $>$  spin-orbit coupling  $>$  crystal field potential, one would preferably include as many optimized CASSCF spin states as possible in the SOC diagonalization. The best possible calculation in this setting would indeed include *all* spin states of the  $4f^n$  manifold in the spin-orbit mixing, corresponding to what in atomic theory is known as complete intermediate coupling.<sup>26</sup>

Note that CASSCF in general employs different molecular orbitals for different states. Calculating a matrix element between any two such states can be computationally expensive in large basis sets, due to the mutual non-orthogonality of the molecular orbitals.<sup>27</sup> The RASSI routine<sup>8,9</sup> of MOLCAS deals efficiently with this problem,

but it is still a computationally demanding task when interaction between a large number of CASSCF states is required. For example, Dy(III), the most studied lanthanide in single-molecule magnetism, has a  $4f^9$  configuration which corresponds to a total of 735 spin states. A complete intermediate coupling calculation would require interaction between 735 CASSCF states. This has so far not been feasible. In fact, in a recent review concerning the application of CASSCF/SO to Ln(III) complexes the authors state that, based on experience, current computer capacities limit the number of states to about 300.<sup>6</sup>

While CASSCF in principle allows individual optimization of CI roots with respect to molecular orbital rotations, this is in practice only feasible for a few of the lowest-energy roots of the CI matrix. When a large number of roots is required, the only viable strategy is to resort to state-averaged CASSCF, whereby the molecular orbitals are optimized to minimize the average energy of the required roots. Thus, within the current application of the CASSCF/SO strategy to Ln(III) complexes, for each  $S$ , a state-averaged CASSCF calculation is performed often including *all* states with spin  $S$  that are possible within the  $4f^n$  manifold, giving equal weight to all states in the average. It should be noted that the molecular orbitals so obtained are completely independent from the CI problem. This can be seen as follows. The CASSCF iterative process involves alternating orbital rotation and CI diagonalization steps. The latter determines the roots and their energy. But if only the average energy of *all* roots is required, then diagonalization is not necessary, because the sum of all eigenvalues is always equal to the sum of all diagonal matrix elements (i.e. the trace of the CI matrix):

$$\sum_{i=1}^{\dim \mathbf{H}_S} E_{S,i} = \text{Tr } \mathbf{H}_S. \quad (1)$$

A CASSCF optimization of this type is thus mathematically equivalent to a minimization of the trace of the CI Hamiltonian matrix with respect to molecular orbital rotations. Since the trace is independent of basis choice, there is no need to build and diagonalize the CI matrix at every iteration. Indeed, one obtains exactly identical results by first performing an SCF minimization of  $\text{Tr } \mathbf{H}_S$  and then, using the orbitals so obtained, a single CI diagonalization to obtain state energies and wave functions. This shows that the orbital optimization is completely decoupled from the CI problem.

The reason that this state-averaging procedure works well is probably that molecular orbital relaxation between states of the  $4f^n$  space is relatively small. In fact, the almost pure atomic nature of the  $4f$  valence shell would suggest that MCSCF calculations are not required. Characteristic for most Ln(III) complexes is indeed the almost complete absence of covalent mixing of  $4f$  atomic orbitals with ligand orbitals. It can therefore be argued that the strong electron correlation problem is essentially an atomic one. In atoms Coulomb repulsion commutes

with both  $S^2$  and  $L^2$  electronic angular momenta, so that if one could start with CSF's with good quantum numbers  $S$  and  $L$  arising from a given  $4f^n$  configuration, i.e. a representation of the Russell–Saunders terms, one would expect such basis to be optimal in order to capture the dominant features of strong electron correlation (static correlation) at the atomic level, or in a few cases after solving very small diagonalization problems for the determination of accurate Russell–Saunders terms as linear combinations of few  $LS$ -symmetry adapted CSF's. It is therefore arguable that pure atomic spin–orbit multiplets characterized by a total angular momentum quantum number  $J$ , obtained by diagonalization of the SOC Hamiltonian on the basis of atomic Russell–Saunders CSF's, would represent the most appropriate guess-states for subsequent molecular calculations, possibly for simple SCF calculations to determine the optimal orbitals in the presence of the crystal field potential. However, current molecular quantum chemistry codes do not work that way and one is typically forced to start from a basis of CSF's that are only spin-symmetry adapted, thus quite far from being atomic states already taking care of on-site correlation.

If this argument is valid, and we are only interested in the properties of the lowest spin–orbit multiplet, we should expect that in the CASSCF/SI–SO approach what captures the relevant electron correlation effects is the attempt to reproduce  $L^2$  eigenfunctions as closely as the rotational symmetry-breaking effect of the ligands allows, pursued via diagonalization of Coulomb repulsion in the basis of the CAS same-spin CSF's. Such attempt would arguably be quite independent of orbital optimization which is instead crucial to represent the symmetry-breaking character of the crystal field electrostatic potential, and consequent splitting of the ground atomic multiplet.

The previous discussion naturally suggests to go one step further and assume that the averaged  $4f$  orbitals will not depend much on the total spin of the wave function either, so that just one set of orbitals can be used to describe the entire  $4f^n$  manifold of states. The result of this simplification is that we can now formulate the CI on a determinantal basis and that the CI on the electrostatic Hamiltonian and on the SOC, which are separated in CASSCF/SI–SO, can now be combined in just one diagonalization step. This approach will be described in the next section.

### III. SIMPLIFIED APPROACH: CAHF/CASCI–SO

The method we propose here consists of two steps. In the first step a set of optimal molecular orbitals is obtained from a suitable configuration-averaged restricted HF-type calculation as detailed in subsection III B. In the second step the optimized orbitals are used to construct *all* Slater determinants of the open  $4f^n$  shell, regardless of which subset was used in the first step to build the aver-

age energy functional. These determinants form the basis for a generalized configuration–interaction type matrix diagonalization which, besides the usual non-relativistic Coulomb repulsion operator, also involves the spin–orbit coupling operator, as detailed in subsection III C.

Configurational-average methodologies have been extensively discussed and applied for many years, since the work of McWeeny who proposed them to treat excited states associated with any number of open shells.<sup>28,29</sup> We also note in passing that, as a cheaper alternative to CASSCF, complete active space configuration interaction (CASCI) based on molecular orbitals determined in a previous step has also been studied by several workers in a variety of contexts.<sup>30–37</sup> Visser et al.<sup>38</sup> applied the idea of configuration-averaged orbitals to a lanthanide crystal-impurity problem in the context of relativistic four-components calculations, which therefore contain spin–orbit coupling from the very start. Their method has never developed, to our knowledge, into a practical non-relativistic *ab initio* approach dedicated to the calculation of crystal field levels and magnetic properties of lanthanide complexes.

#### A. Hamiltonian

The Hamiltonian that we use in the present paper is identical to that used for CASSCF/SI–SO calculations in MOLCAS.<sup>9</sup> It is given by the second order Douglas–Kroll–Hess (DKH) scalar Hamiltonian, combined with the usual non-relativistic Coulomb electron repulsion operator and an effective one-electron atomic mean-field (AMFI) approximation of the DKH no-pair spin–orbit operator.<sup>8,39</sup> A detailed description of this Hamiltonian can be found in Ref.<sup>40</sup>.

We have implemented configuration-averaged Hartree–Fock (CAHF) and spin–orbit-inclusive complete-active space configuration interaction (CASCI–SO) modules in a local development code, CERES (*Computational Emulator of Rare Earth Systems*), which is based on the open-shell version<sup>41</sup> of the SYSMO software.<sup>42</sup> Since in SYSMO the integrals of the DKH operators in the atomic basis set are not available, all integrals are computed using the SEWARD program of MOLCAS 8.0,<sup>9</sup> and read into CERES to be used by our CAHF and CASCI–SO modules, which are described in the next sections.

#### B. Configuration-averaged Hartree–Fock (CAHF) orbitals

In order to obtain a set of molecular orbitals (MO) for the subsequent CI calculation we minimize the average energy of the states of the  $4f^n$  configuration.<sup>28</sup> There are several ways one might choose to do this. For instance, we could build an average-energy functional over all Slater determinants with a constant  $M_S$  projection of the spin angular momentum. Such approach turns out to be rather useful, e.g. for debugging purposes. In fact,

when  $M_S = S_{\max}$ , the energy functional is equivalent to that minimized during a state-averaged CASSCF calculation performed with as many roots as there are  $S = S_{\max}$  states within the  $4f^n$  configuration (see Eq. (1)), and thus the orbitals obtained via this approach should be equivalent to those obtained via a state-averaged CASSCF calculation with MOLCAS. Moreover, for any other  $M_S$  value our configuration-averaged approach optimizes orbitals by mixing two or more spin-manifolds. Clearly, such orbitals are not equivalent to any of the state-averaged CASSCF optimized orbitals, and it is thus an interesting question whether this can lead to significant discrepancies between the two approaches. Finally, we can average over all  $M_S$  spin manifolds and simply obtain a fully-averaged SCF problem within the  $4f^n$  configuration, in the spirit of the old McWeeny proposal,<sup>28</sup> which, if our reasoning is correct, should yet again lead to nearly atomic 4f-like orbitals with no appreciable discrepancies from the SA-CASSCF methodology.

McWeeny has treated the general case of configurational averaging (see, for example, Ref.<sup>29</sup>, §§6.5–6.6). We briefly present here the special case of  $M_S$ -configuration-averaging, and then generalize the results to those reported by McWeeny. We use McWeeny's density matrix notation.

Let us consider a system with one closed and one open shell, having  $n_1$  spatial orbitals in the closed shell (or  $n_1$  inactive orbitals),  $n_2$  spatial orbitals in the open shell (or  $n_2$  active orbitals). Let  $n_A$  be the number of active electrons, with  $n_\alpha$  spin-up and  $n_\beta$  spin-down electrons ( $n_A = n_\alpha + n_\beta$ ), thus with fixed  $M_S = 1/2(n_\alpha - n_\beta)$  value. Averaging the electrostatic Hamiltonian over the  $\binom{n_2}{n_\alpha} \binom{n_2}{n_\beta}$  Slater determinants that can be formed by occupying the  $n_2$  active orbitals with  $n_\alpha$  spin-up electrons and  $n_\beta$  spin-down electrons we obtain the energy functional:

$$E_{\text{av}}^{M_S} = \nu_1 \sum_i^{n_1} h_i + \frac{\nu_1^2}{2} \sum_{i,j}^{n_1} (J_{ij} - \frac{1}{2} K_{ij}) \quad (2a)$$

$$+ \nu_1 \nu_2 \sum_i^{n_1} \sum_u^{n_2} (J_{iu} - \frac{1}{2} K_{iu}) \quad (2b)$$

$$+ \nu_2 \sum_u^{n_2} h_u + \frac{\nu_2^2}{2} \sum_{u,v}^{n_2} (\lambda_J^{M_S} J_{uv} - \lambda_K^{M_S} K_{uv}). \quad (2c)$$

where  $\nu_1 = 2$ ,  $\nu_2 = \frac{n_A}{n_2}$  are the (average) occupations of the two sub-shells, indices  $i, j$  run over the inactive space, indices  $u, v$  run over the active space, and the Coulomb ( $J_{uv}$ ) and exchange ( $K_{uv}$ ) integrals for the active space are weighted by the  $M_S$ -dependent coefficients:

$$\lambda_J^{M_S} = \frac{n_2 n_A (n_A - 1) - 2 n_\alpha n_\beta}{n_A^2 (n_2 - 1)} \quad (3)$$

$$\lambda_K^{M_S} = \frac{n_2 n_A (n_A - 1) - 2 n_2 n_\alpha n_\beta}{n_A^2 (n_2 - 1)}$$

This expression can be rewritten in terms of density

and integral matrices on the atomic basis

$$E_{\text{av}} = \nu_1 \text{Tr}[\mathbf{R}_1(\mathbf{h} + \frac{1}{2}\mathbf{G}_1)] + \nu_2 \text{Tr}[\mathbf{R}_2(\mathbf{h} + \frac{1}{2}\mathbf{G}_2)], \quad (4)$$

where  $\mathbf{R}_i = \mathbf{T}_i \mathbf{T}_i^\top$  is the density matrix of shell  $i$ , whose LCAO coefficients are contained in the columns of  $\mathbf{T}_i$ ,  $\mathbf{h}$  is the matrix of the one-electron Hamiltonian, and

$$\mathbf{G}_1 = \nu_1 \mathbf{G}(\mathbf{R}_1) + \nu_2 \mathbf{G}(\mathbf{R}_2) \quad (5)$$

$$\mathbf{G}_2 = \nu_1 \mathbf{G}(\mathbf{R}_1) + \nu_2 \mathbf{G}^{M_S}(\mathbf{R}_2)$$

are Coulomb-exchange matrices, with

$$\mathbf{G}(\mathbf{R}) = \mathbf{J}(\mathbf{R}) - \frac{1}{2}\mathbf{K}(\mathbf{R}) \quad (6)$$

$$\mathbf{G}^{M_S}(\mathbf{R}) = \lambda_J^{M_S} \mathbf{J}(\mathbf{R}) - \lambda_K^{M_S} \mathbf{K}(\mathbf{R}),$$

and

$$\mathbf{J}(\mathbf{R})_{\alpha\beta} = \sum_{\delta\gamma} \mathbf{R}_{\delta\gamma} \langle \gamma\alpha | \delta\beta \rangle \quad (7)$$

$$\mathbf{K}(\mathbf{R})_{\alpha\beta} = \sum_{\delta\gamma} \mathbf{R}_{\delta\gamma} \langle \gamma\alpha | \beta\delta \rangle$$

the usual Coulomb and exchange matrices, respectively. Greek letters denote basis set functions.

We are also interested in optimizing the energy functional originally proposed by McWeeny, arising from averaging over the full set of Slater determinants that can be obtained in the chosen active space, regardless of the spin-projection quantum number  $M_S$ . This can be easily recovered by multiplying  $\lambda_J^{M_S}$  and  $\lambda_K^{M_S}$  in Eqs. (3) by the number of Slater determinants  $\binom{n_2}{n_A/2+M_S} \binom{n_2}{n_A/2-M_S}$  with constant  $M_S$ , summing over all possible  $M_S$ , and dividing by the total number of Slater determinants. This leads to:

$$\bar{\lambda}_J = \frac{\sum_{M_S} \binom{n_2}{\frac{n_A}{2}+M_S} \binom{n_2}{\frac{n_A}{2}-M_S} \lambda_J^{M_S}}{\sum_{M_S} \binom{n_2}{\frac{n_A}{2}+M_S} \binom{n_2}{\frac{n_A}{2}-M_S}} = \frac{2}{\nu_2} \frac{(n_A - 1)}{(2n_2 - 1)}$$

$$\bar{\lambda}_K = \frac{\sum_{M_S} \binom{n_2}{\frac{n_A}{2}+M_S} \binom{n_2}{\frac{n_A}{2}-M_S} \lambda_K^{M_S}}{\sum_{M_S} \binom{n_2}{\frac{n_A}{2}+M_S} \binom{n_2}{\frac{n_A}{2}-M_S}} = \frac{1}{\nu_2} \frac{(n_A - 1)}{(2n_2 - 1)} \quad (8)$$

which determines a modified energy functional, given by a modified Eq. (2), where the average electron-electron repulsion term within the active space (i.e., last term in the last line in Eq. (2)) is modified using Eq. (8), thus becoming:

$$\nu_2 \frac{(n_A - 1)}{(2n_2 - 1)} \sum_{u,v}^{n_2} (J_{uv} - \frac{1}{2} K_{uv}). \quad (9)$$

The energy functional Eq. (2), or equivalently that originally proposed by McWeeny that can be obtained

from Eq. (9), is akin to the energy functional arising in the restricted open-shell HF (ROHF) theory.<sup>29</sup> Thus it can be easily shown that a sufficient condition to minimize Eq. (2) or Eq. (4) is to build the density matrices for inactive and active spaces from the converged self-consistent eigenfunctions of an effective Fock-like Hamiltonian:

$$\mathbf{F}_{\text{eff}} = a\tilde{\mathbf{R}}_2\mathbf{F}_1\tilde{\mathbf{R}}_2 + b\tilde{\mathbf{R}}_1\mathbf{F}_2\tilde{\mathbf{R}}_1 + c\tilde{\mathbf{R}}_3(\nu_1\mathbf{F}_1 - \nu_2\mathbf{F}_2)\tilde{\mathbf{R}}_3 \quad (10)$$

where  $\mathbf{F}_i = \mathbf{h} + \mathbf{G}_i$ ,  $\tilde{\mathbf{R}}_i = \mathbf{1} - \mathbf{R}_i$ , and  $a$ ,  $b$  and  $c$  are arbitrary real non-zero parameters that can be adjusted to improve convergence of the SCF process. This procedure has been implemented via a simple modification of the open-shell SYMO code<sup>41</sup>, by modifying the mean-field repulsion potential within the active space by Eqs. (3) or Eqs. (8), which enter Eq. (10) via the G-matrix  $\mathbf{G}_2$  in Eq. (5). For the time being the only tools we have implemented to achieve convergence of the configuration-averaged SCF process are a direct inversion of the iterative subspace (DIIS) algorithm,<sup>43</sup> and level shifters for the open and virtual shells.<sup>44</sup>

### C. Spin-orbit-including complete active space configuration interaction (CASSCF-SO)

The CAHF orbitals are now used to set up the full configuration interaction calculation in the determinantal basis of the open shell. Since there are 7 spatial 4f orbitals and  $n$  electrons distributed among them, the dimension of the CI secular matrix is  $\binom{14}{n}$ . The largest dimension occurs for  $n = 7$  and is 3432. As this is a relatively small number, diagonalization of the CI matrix is fast.

The CI routine that we have implemented is based on the  $\sigma$ -algorithm of Olsen *et al.*<sup>45</sup> for the scalar (spin-conserving) part of the Hamiltonian (i.e., the scalar one-electron plus interelectronic Coulomb repulsion terms). We also need to include the CI matrix elements of the SOC operator, which is not spin-conserving.

The AMFI SOC operator can generally be written as

$$H^{\text{SO}} = \sum_i \mathbf{t}(i) \cdot \mathbf{s}(i), \quad (11)$$

where the summation is over all electrons, and  $\mathbf{t}$  is a function of space only. In second quantization this gives

$$H^{\text{SO}} = \frac{1}{2} \sum_{u,v} [t_{uv}^z a_{u\alpha}^\dagger a_{v\alpha} - t_{uv}^z a_{u\beta}^\dagger a_{v\beta} + (t_{uv}^x - it_{uv}^y) a_{u\alpha}^\dagger a_{v\beta} + (t_{uv}^x + it_{uv}^y) a_{u\beta}^\dagger a_{v\alpha}], \quad (12)$$

where  $\mathbf{t}_{uv}$  are the AMFI integrals, transformed to the active molecular orbital basis. The first two terms are spin-conserving, and can be handled by the scalar CI algorithm.<sup>45</sup> The third and the fourth term introduce spin flips and in order to include these we have supplemented the original algorithm with routines that handle single excitations from  $\alpha$  to  $\beta$  spin orbitals and vice versa.

## IV. APPLICATION

This section presents results of calculations on three isostructural complexes:  $[\text{Ln}(\text{acac})_3(\text{H}_2\text{O})_2]$ ,  $\text{Ln} = \text{Dy}$ ,  $\text{Ho}$ ,  $\text{Er}$ .<sup>46</sup> We compare the CASSCF/SI-SO method with the CAHF/CASCI-SO method.

We performed single-point calculations on all three complexes, using the crystallographic structures.<sup>46</sup> ANO-RCC basis sets<sup>47</sup> were used on all atoms, contracted to [9s8p6d4f3g2h] for Dy, Ho, Er, [3s2p1d] for C and O, and [2s1p] for H.

CASSCF/SI-SO calculations were done with MOLCAS 8.0.<sup>9</sup> The active space consists of the seven Ln 4f orbitals, and is occupied by 9 electrons for Dy, 10 electrons for Ho, and 11 electrons for Er. These occupations correspond to the trivalent oxidation state and give rise to a ground spin-orbit multiplet with total angular momentum  $J = 15/2$  for Dy(III),  $J = 8$  for Ho(III), and  $J = 15/2$  for Er(III). (Within the single Russell-Saunders term approximation, these correspond to  ${}^6\text{H}_{15/2}$  for Dy(III),  ${}^5\text{I}_8$  for Ho(III), and  ${}^4\text{I}_{15/2}$  for Er(III)). Crystal field splitting of the  $J$  multiplets results in eight low-lying Kramers doublets (KD's) for the Dy and Er compounds. The ground  $J$  multiplet of the Ho compound, being an even-electron system, splits into seventeen non-degenerate states. State-averaged (SA) CASSCF optimizations were done on the average energy of all states belonging to the highest spin, *viz.* 21  $S = 5/2$  states for Dy, 35  $S = 2$  states for Ho, and 35  $S = 3/2$  states for Er. The resulting wave functions were spin-orbit coupled with the RASSI module of MOLCAS. We chose not to include states of lower spin in the spin-orbit coupling calculation for two reasons: First, as mentioned in Section II, it is computationally not feasible to include all spins of the 4f<sup>9</sup> manifold of Dy(III) in a RASSI calculation (this goes for the 4f<sup>10</sup> manifold of Ho(III) as well). In practice, one resorts to an approximation, either by discarding states above a certain cutoff energy, or by just including the highest-spin states only.<sup>6</sup> Second, this allows to assess the influence of SOC mixing with states of lower spin, by comparison with the CASCI-SO results.

CAHF/CASCI-SO calculations were done following the method described in Section III. Two different types of HF averaging were considered to obtain the molecular orbitals: in the first, averaging was done over all determinants with maximum spin projection  $M_S$ , using the  $\lambda$  coefficients in Eq. (3). In the second type averaging was done over *all* determinants, using the  $\bar{\lambda}$  coefficients in Eq. (8).

Magnetic g-factors were calculated for each Kramers doublet of the Dy and Er complexes.<sup>48,49</sup> The Ho complex is an even-electron system and as such has no Kramers doublets. Nevertheless, it is sometimes possible to find two quasi-degenerate states and treat them as a pseudo-doublet, for which g-factors can be calculated. This has been done for the two lowest states of the Ho complex (Table III). Note that such pseudo-doublets have only

TABLE I.  $[\text{Ln}(\text{acac})_3(\text{H}_2\text{O})_2]$ : Comparison of total energies, shifted by  $-13328$  Hartree for Dy,  $-13787$  Hartree for Ho, and  $-14256$  Hartree for Er. GS = ground state energy.

Ion		SA-CASSCF	CAHF	CAHF
		on $S_{\text{max}}$	on $M_S = S_{\text{max}}$	on all $M_S$
Dy	$E_{\text{av}}$	-1.021652	-1.021652	-0.777037
		CASSCF		
	GS	-1.057170	-1.057170	-1.055993
		SI-SO		
	GS	-1.079553	-1.086042	-1.084697
Ho	$E_{\text{av}}$	-0.477551	-0.477551	-0.327231
		CASSCF		
	GS	-0.559519	-0.559519	-0.558906
		SI-SO		
	GS	-0.589286	-0.595589	-0.594871
Er	$E_{\text{av}}$	-0.866271	-0.866271	-0.789330
		CASSCF		
	GS	-0.949870	-0.949870	-0.949656
		SI-SO		
	GS	-0.982882	-0.986258	-0.985998

one non-zero principal g-factor.<sup>50</sup>

Table I presents calculated average and ground state energies, the latter both with and without inclusion of SOC. Note that the SOC-free energies in columns 1 and 2 are identical. This confirms the equivalence of SA-CASSCF and CAHF orbitals for the high-spin subspace, predicted by Eq. (1).

The calculated relative energies and magnetic g-factors are summarized in Tables II–IV. It is clear that there is minimal difference between the results generated by the three methods. The largest changes are observed when including all spin states in the spin-orbit coupling, as opposed to the high-spin states only. Smaller changes are observed when using orbitals averaged over all states, as opposed to orbitals averaged over the high-spin states only.

## V. CONCLUSION

We have investigated the application of the CAS-SCF/SI-SO *ab initio* method to the calculation of crystal field splitting and magnetic anisotropy in complexes of trivalent lanthanide ions. The two main ingredients of this method are: (i) Coupling of Slater determinants into Russell-Saunders-like terms by configuration interaction in the active space  $4f^n$ ; (ii) Coupling of those terms into  $J$ -like multiplets by spin-orbit state interaction. CASSCF performs step (i) but uses state-dependent molecular orbitals. This complicates step (ii) because the SI-SO program has to calculate matrix elements between states expressed in mutually non-orthogonal or-

TABLE II.  $[\text{Dy}(\text{acac})_3(\text{H}_2\text{O})_2]$ : Calculated relative energies and g-factors of the Kramers doublets corresponding to the crystal-field split  $J = 15/2$  ground multiplet.

Doublet	Energy/ $\text{cm}^{-1}$	$g_1$	$g_2$	$g_3$
SA-CASSCF/SI-SO ( $S = 5/2$ )				
1	0.0	0.01	0.01	19.56
2	156.4	0.26	0.45	15.70
3	234.8	2.02	2.87	11.28
4	289.5	2.27	5.87	7.01
5	323.3	2.12	4.25	13.84
6	417.9	0.01	0.13	16.28
7	477.7	0.04	0.08	18.84
8	539.7	0.01	0.02	19.22
CAHF ( $M_S = 5/2$ )/CASSCF-SO				
1	0.0	0.01	0.01	19.44
2	154.0	0.26	0.45	15.60
3	231.9	1.92	2.75	11.22
4	285.8	2.42	6.02	6.99
5	319.1	2.05	4.13	13.66
6	410.8	0.00	0.13	16.21
7	468.9	0.04	0.07	18.78
8	529.8	0.01	0.02	19.14
CAHF (all $M_S$ )/CASSCF-SO				
1	0.0	0.01	0.01	19.43
2	155.0	0.25	0.43	15.59
3	234.2	1.87	2.68	11.23
4	288.5	2.40	6.05	6.97
5	321.2	2.05	4.22	13.60
6	413.3	0.01	0.13	16.23
7	471.8	0.04	0.07	18.79
8	533.3	0.01	0.02	19.14

bitals. Based on the fact that “4f molecular orbitals” in  $\text{Ln}(\text{III})$  complexes are almost pure atomic 4f orbitals we have suggested that significant state-dependence of the CASSCF molecular orbitals is not expected. This is corroborated by the already common practice of state-averaging CASSCF over a large number of  $4f^n$  states. If so, a single set of 4f-configuration-averaged orbitals may be used to represent all states. As a result, steps (i) and (ii) may be combined in a convenient single diagonalization on the Slater determinant basis.

## ACKNOWLEDGMENTS

W.V.d.H. thanks the University of Melbourne for a McKenzie Postdoctoral Fellowship. A.S. acknowledges financial support from the Australian Research Council, through a Discovery Grant, project ID: DP150103254.

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TABLE III.  $[\text{Ho}(\text{acac})_3(\text{H}_2\text{O})_2]$ : Calculated relative energies of the states corresponding to the crystal-field split  $J = 8$  ground multiplet. The calculated g-factors are those of the pseudo-doublet consisting of states 1 and 2.

	SA-CASSCF/ SI-SO ( $S = 2$ )	CAHF ( $M_S = 2$ )/ CASSI-SO	CAHF (all $M_S$ )/ CASSI-SO
$g_1$	0.00	0.00	0.00
$g_2$	0.00	0.00	0.00
$g_3$	17.23	17.12	17.16

  

State	Energy/cm <sup>-1</sup>		
1	0.0	0.0	0.0
2	4.2	4.0	3.9
3	34.9	33.2	33.6
4	45.0	42.7	43.0
5	101.4	96.1	96.5
6	125.8	118.8	119.2
7	146.1	138.1	138.4
8	162.5	153.5	154.1
9	177.6	168.3	168.4
10	209.0	197.7	197.5
11	220.1	208.1	208.1
12	222.8	210.6	210.8
13	230.9	218.5	218.3
14	255.6	242.0	242.2
15	264.3	250.1	250.0
16	293.9	277.6	277.4
17	295.0	278.6	278.4

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TABLE IV.  $[\text{Er}(\text{acac})_3(\text{H}_2\text{O})_2]$ : Calculated relative energies and g-factors of the Kramers doublets corresponding to the crystal-field split  $J = 15/2$  ground multiplet.

Doublet	Energy/cm <sup>-1</sup>	$g_1$	$g_2$	$g_3$
SA-CASSCF/SI-SO ( $S = 3/2$ )				
1	0.0	0.65	1.88	14.43
2	29.6	1.92	3.48	12.24
3	70.4	1.74	4.41	9.45
4	87.5	0.27	3.64	10.85
5	135.3	0.19	3.69	10.37
6	179.1	1.56	3.82	10.99
7	252.2	0.15	2.64	11.53
8	296.6	0.63	2.11	15.26
CAHF ( $M_S = 3/2$ )/CASSI-SO				
1	0.0	0.57	1.68	14.62
2	29.2	1.81	3.21	12.59
3	70.9	1.91	4.24	9.62
4	89.0	0.23	4.01	10.39
5	134.3	0.23	3.47	10.40
6	179.0	1.65	3.80	11.03
7	253.3	0.29	2.48	11.68
8	299.9	0.58	1.88	15.38
CAHF (all $M_S$ )/CASSI-SO				
1	0.0	0.56	1.69	14.62
2	28.7	1.77	3.20	12.62
3	70.6	1.95	4.23	9.64
4	88.8	0.21	4.10	10.34
5	133.8	0.23	3.46	10.40
6	178.4	1.65	3.79	11.07
7	252.4	0.32	2.46	11.70
8	299.2	0.57	1.85	15.39

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